Renewable and Sustainable Energy Reviews 14 (2010) 3178–3184

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Design methods for large scale dye-sensitized solar modules and the progress of stability research

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ARTICLE INFO

Article history:
Received 13 May 2010
Accepted 16 June 2010

Keywords:
Dye-sensitized solar cells
Large scale modules
Serial modules
Parallel modules
Stability

ABSTRACT

In this article, design methods for large scale dye-sensitized solar modules were introduced. The latest results about the experimental and commercialized research on different kinds of large scale dye-sensitized solar modules were reviewed. Indoor and outdoor tests carried out to identify the stability of dye-sensitized solar cells and large scale modules were presented according to IEC international standards. The problems encountered on the progress of DSC stability research were analyzed and future development targets were expected.

Contents

1. Introduction

As one kind of thin film cells, dye-sensitized solar cell (DSC) has become a research focus because of the advantages in simple manufacture process, low cost and appearance variety. Especially after the nano-film concept had been introduced to DSC fabrication

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1364-0321/$ – see front matter
doi:10.1016/j.rser.2010.06.019

process and a solar energy conversion efficiency of 7.1% (Air Mass/AM 1.5, 750 W/m^2) had been achieved by Grätzel and O'Regan of Swiss Federal Institute of Technology (EPFL) in 1991 [1], much more DSC efficiency records had been reported for single cells on small area (<1 cm^2) with the improvements in materials and technologies. In 2004, Prof. Grätzel's group achieved an efficiency record of 11.04% (AM 1.5, 1000 W/m^2) by enhancing the self-assembly progress of the N3-dye on TiO_2 thin film network to form a compact dye monolayer and resulting in a remarkable improvement of the cell voltage due to a reduction in dark current [2,3]. Sharp Corporation investigated the improvement of DSC performance derived from the reduced series resistance using TiO_2 electrodes with high haze. The efficiency of 10.4% (aperture area: 1 cm^2) [4] and 11.1% (aperture area: 0.219 cm^2) [5,6] were reported in 2005 and 2006 respectively under standard sunlight, which were confirmed by a public test center, the Research Center for Photovoltaics at the National Institute of Advanced Industrial Science and Technology (AIST) in Japan. The above experimental efficiency values of DSCs are comparable to those of commercialized amorphous silicon thin film solar cells. While, along with the up-scaling of DSC, the electrons transferred in the nanocrystalline net of the cell will more likely to recombine with electron acceptors, causing current loses [7]. The probability for the occurrence of leaking holes, scratches on TiO_2 anode and the impurity defects, which are caused by simple sandwich technique, will multiply. The open circuit voltage and fill factor of DSC will decrease rapidly with the increase of shunt current [8]. If the design methods and techniques of DSC are not optimized appropriately, the efficiency of the cell is likely lower than 1% when the size is up to 10 cm × 10 cm [9]. On the other hand, as liquid electrolyte is used, encapsulation problems and instability have become the obstacles in the progress of DSC application. Therefore, the design methods for large scale DSC modules and the stability research have attracted much more attentions of research institutes and commercial companies worldwide.

In this article, the design methods for large scale DSC modules were introduced. The latest results about the experimental and commercialized research on different kinds of large scale DSC modules were reviewed. As the research on DSC is currently on experimental stage, there are no specific international standards prepared to guide the stability research. Indoor and outdoor tests carried out to identify the stability of DSCs and the large scale modules were presented according to International Electrotechnical Commission (IEC) standards for thin film photovoltaic modules and crystalline silicon photovoltaic modules. The problems encountered on the progress of DSC stability research were analyzed and future development targets were expected.

2. Design methods for large scale DSC modules

In aspect of up-scaling of DSC, individual cells have to be connected into modules. The relatively high sheet resistance of the transparent conductive coating (TCO) like SnO_2:F (FTO) (usually 10/square) used as the current collector limits the width of the individual cells to less than 1 cm [9]. One method to reduce ohmic resistance losses in a module is to interconnect many parallel single cells in series. Three types of series-connected design can be distinguished: Z-, W-type and a monolithic connection of individual cells. An alternative way is to apply metals of low resistivity like Ag, Cu, Ni, Ti, etc. as the current collector grid on substrates of DSC modules, in order to increase the collect efficiency of electrons by reducing the distance of electrons transfer, quite similar to silicon technology.

2.1. Serial DSC modules

2.1.1. Z-type serial DSC module

Z-type serial design is usually applied in the fabrication of amorphous silicon solar cells of which glass/metal, plastic/metal, glass/plastic and plastic/plastic can be used for substrates, and consists of two opposing electrodes with the interconnection between neighboring cells provided by a conductor medium [10], as shown in Fig. 1. Sealing barrier is needed to protect the conductor medium from decaying under the action of iodide ion. Thus, each single cell in the module formed a close compartment i.e. mass transport of the electrolyte between neighboring cells must be prevented. As single cells in a module have different electrochemical potentials under open-circuit conditions when illuminated. If there was a possibility for ion exchange between the redox electrolytes of neighboring cells, the redox couple would separate. This process is often called photophoresis. During the photophoresis the electrical parameters of the module would slowly drop. Electrolyte is filled into a module through the holes drilled on the substrate of each single cell. Freiburger Materials Research Centre (FMF), Germany, fabricated the Z-type serial module with glass frit as seal and Ag as conductor medium. This design was unique compared to normal Z-type in two aspects. First, in order to avoid the drilling and sealing of a very large number of holes in glass substrate, an electrolyte canal was integrated in the module to distribute the dye and electrolyte to all cell compartments, with only two holes left in the electrolyte canals. Second, the module was colored and filled with electrolyte via the two holes after the fusing process because glass frit has a high processing temperature (600 °C) at which dye would decompose. Modules of 30 cm × 30 cm totally, 505.5 cm^2 actively, were fabricated with 29 single cells of 7 mm width in series connection by a separation of 2 mm. Active efficiency of 3.5% was reported under standard sunlight at 38 °C in 2006 [11]. In the Sustainable Technology International (STI) design of Z-type serial module, a new type of interconnection was used to act as not only the conducting medium but also as the barrier between single cells, as disclosed in of STI Patent [12]. The scheme was shown in Fig. 2. This design was based on the invention of the interconnection with low resistance and tough anti-erosion performance in electrolyte. The advantage of Z-type serial design is high voltage output. The disadvantage is the low active area and efficiency resulting from the relatively complex construction and high series resistance of the three layers of seal/conductor/seal interconnection which were improved by the innovative design by STI.

2.1.2. W-type serial DSC module

Compared to Z-type serial DSC module, which series-junction is fabricated by the conductor medium, W-type serial DSC module avoids interconnections by entailing neighbor single cells being alternate bias and still requires separation of the cells by an effective seal [13], as shown in Fig. 3. The advantage of this design is simple, apparently, which also causes the disadvantages of this design. As there are differences between the currents of the single cells illuminated from the working electrode side (front side,

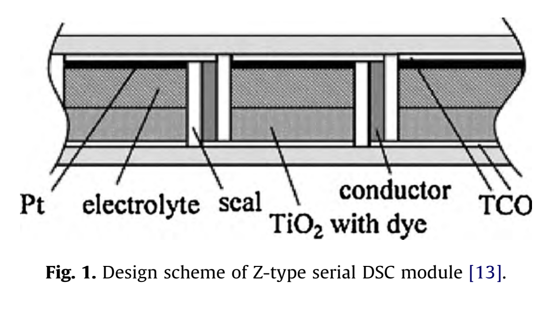


Fig. 1. Design scheme of Z-type serial DSC module [13].

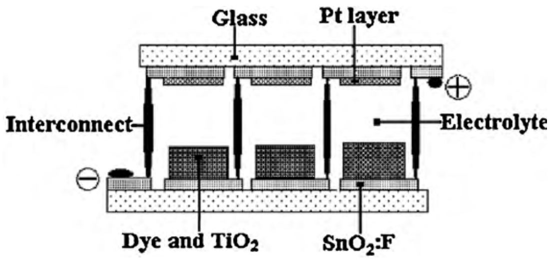


Fig. 2. Design scheme of Z-type serial DSC module of STI [10].

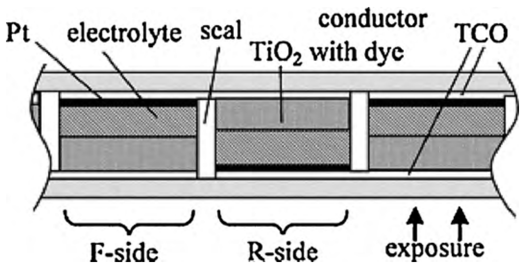


Fig. 3. Design scheme of W-type serial DSC module [13].

F-side) and the counter-electrode side (reverse side, R-side), resulting not only from the different light transmittance of the two sides but also from the absorption of the light by the triiodide ion in the electrolyte. So this design provides about 80% of the performance of a similar Z-type serial module [14]. In order to solve the problem of mismatch between the neighbor cells, methods like adjusting the transmittance and width of the two electrodes, and the concentration of the triiodide ion in the electrolyte were put forwarded by Sharp Corporation, Japan, though these measures will cause more complex of fabrication. In 2009, an efficiency of 8.29% totally, 9.3% actively, was reported by Sharp on a W-type DSC module of 5.0 cm $\times$ 5.3 cm with active area up to 85%, as measured by the AIST public test center [13,15].

2.1.3. Monolithic serial DSC module

Monolithic serial DSC module is also called Kay cell as invented by Dr. Andreas Kay of EPFL. He reported the efficiency of 5.29% on a monolithic module with 6 single cells of 4.7 cm $\times$ 0.7 cm serial connected, as well as 6.67% on a 0.4 cm^2 small monolithic cell, which were tested by National Renewable Energy Laboratory (NREL) in 1996 [16]. Fig. 4 and Fig. 5 show the design scheme and continuous process for the fabrication of monolithic serial DSC module, respectively. Unlike Z- and W-type serial design, only one substrate is used to fabricate the monolithic serial module on which working electrode, electrical insulator and counter-electrode/back substrate are printed. So the cost of this design will be reduced over half [17]. The electrical insulator is designed to avoid the direct ohm contact between working electrode and counter-electrode. On the other hand, the electrical insulator must be porous to provide passway for ionic transport. Rutile TiO_2 was first

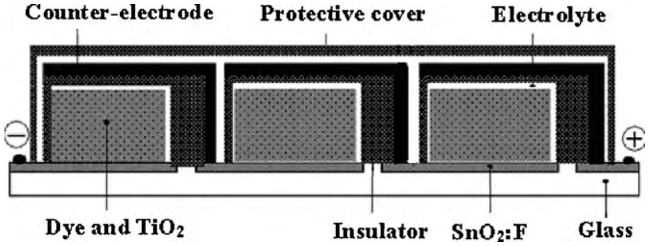


Fig. 4. Design scheme of monolithic serial DSC module [10].

used to act as the electrical insulating material as well as light reflecting layer by Dr. Andreas Kay. ZrO_2 was also used as electrical insulator by STI [18]. These electrical insulating materials are all opaque. In order to overcome this defect, SiO_2 with refractive index (about 1.5) quite close to the electrolyte was tried by Aisin, Japan in 2009 [19]. The back substrate enables both catalysis function for the redox reaction and serial connection between the single sells. The back electrode choosed by STI was carbon in different morphological ratios, doped to enhance bonding to the substrate which is still on of process optimization. New structured nanomaterials (e.g. nanochannels) also work as alternatives of carbon [13]. For the transparent monolithic module made by Aisin, carbon was displaced by a screen-printing paste composed of Pt-loaded In_2O_3:Sn nanoparticles (70 nm) dissolved in ethyl-cellulose and terpineol. The dye is usually applied after all materials are printed, so the dye usage is higher than in the Z-type serial design. As no rigid separators are required to maintain constant cell thickness this design is preferred to fabricate the flexible DSC module with continuous process. Whereas, the low efficiency caused by high series resistance has been a limiting factor to limit its application under high solar radiation conditions.

2.2. Parallel DSC modules

For all types of serial DSC module, single cells must be insulated and serial connected causing a complex fabrication process, high serial resistance and low efficiency. Moreover, series connection should be fabricated between working electrode side and counter-electrode side, so precise process is required to maintain preferred ohmic contact. In contrast, a comparative simple fabrication process is used to fabricate large scale DSC modules. In this design the parallel grids utilizing conductive fingers to collect current are printed on the two substrates separately, quite similar to silicon technology. Though invented early in 1995 [14], the research work on this design was suspended as metals trailed for the grid like Ag, Au, Cu, Al, and Ni were all easy to be corroded by the iodide electrolyte. Until the new coatings like polymer, glass frit, ceramic glazes, etc. were applied to protect grids successfully, parallel DSC module has been realized as an alternative design for large scale DSC module.

From 2002 until 2004, a consortium consisting of four universities (EPFL, Imperial College, Cracow University and Freiburger Materials Research Center), three research institutes (ECN Solar Energy, Fraunhofer ISE, IVF Industrial Research and Development Corporation) and one industrial partner (Greatcell Solar SA) had cooperated in the framework of a European project called NANOMAX. The activities in NANOMAX were focused on demonstrating new strategies for DSC cell concepts, cell materials and fabrication protocols with the aim to increase the efficiency to >12% under standard test conditions (AM 1.5, 1000 W/m^2) and the long-term stability [20]. The research institutes of the consortium (ECN, FMF/ISE, IVF) followed a common approach for the processing of DSC on so-called 'masterplates' in a semi-automated processing line installed in ECN with a common design and size to create a basis for comparability of testing conditions and a comparable format for measurement and processing data. One kind of the classic masterplate was fabricated with size of 10 cm $\times$ 10 cm totally, 68 cm^2 actively, using silver grids as current collection which was protected by Surlyn or Bynel. Fig. 6 shows the picture of a framed masterplate DSC module in parallel design. In contrast to serial designs where multiple holes are needed to fill the electrolyte, only one electrolyte filling hole was drilled on the top central of the plate in this design. The electrolyte was pressed in the plate and dispersed by centrifugal force. The active efficiency of this classic 10 cm $\times$ 10 cm-sized module was up to 5.9%, quite close to the maximum efficiency, 6%,

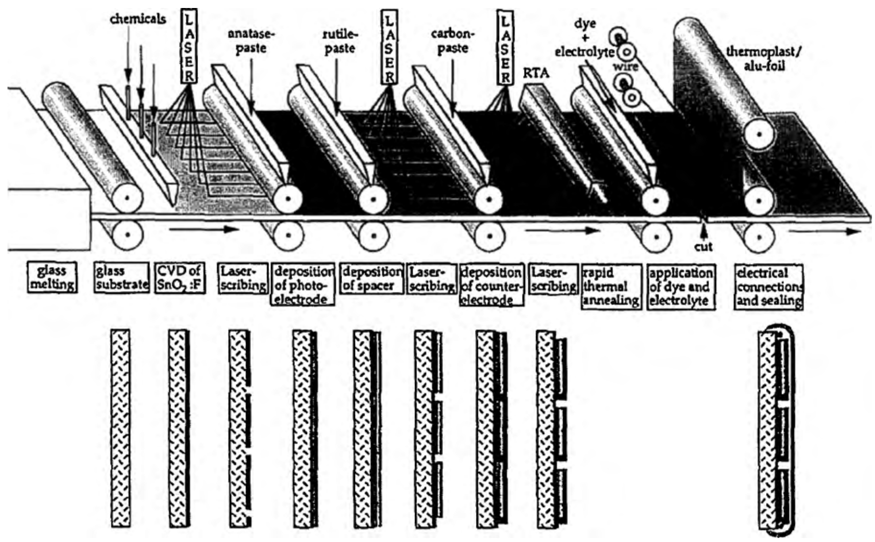


Fig. 5. Continuous process for the fabrication of monolithic serial DSC module [16].

of the single 2.5 cm^2-sized cells fabricated by the same process. This demonstrates that the up-scaling technology do not show remarkable impact on the performance of the cells. The overall yield for a series of 27 modules (10 cm × 10 cm) was 96%, while 84% (22 of the remaining 26 modules) generated cell efficiencies within 7% deviation from the average value (4.3%). The results show the baseline is good in terms of process reliability and yield [9,21].

Another kind of the masterplate fabricated on the semi-automated processing line comprised of five single cells with an overall size of 10 cm × 7.5 cm. The size of the single cells was 5.0 cm × 0.5 cm or 5.0 cm × 0.8 cm. As these single cells were fabricated by the same manufacturing process, this kind of masterplate was used as the main research vehicle for testing new materials, components and stability of DSC [22].

The up sizing research in Fujikura, Japan disclosed that nickel was appropriate for current correcting lines of DSC because of its long lifetime in a redox electrolyte, and low dark current density to the electrolyte. The substrate with low sheet resistance (0.28 Ω/square) as well as high transmittance (66%) was fabricated with nickel grids formed by an electroplating process and $F:SnO_2$/$Sn:In_2O_3$ (FTO/ITO) double layered transparent conductive oxides. The efficiency of 4.3% totally, 5.1% actively, was obtained on a 100 mm × 100 mm-sized large module [23].



Fig. 6. The picture of a framed masterplate DSC module in parallel design with total area of 10 cm × 10 cm [9].

The Institute of Plasma Physics, Chinese Academe of Science (IPP, CAS), has been performing the fundamental research on the theories of DSC for many years. In recent years, the mechanisms and technologies for large scale DSC module fabrication were also explored by IPP and achievements were gained at top level in the world [10,24–32]. The design scheme of the parallel DSC module in IPP was shown in Fig. 7. The panel of 45 cm × 80 cm in size was assembled by the modules of 15 cm × 20 cm which are active in 187.2 cm^2, with a total efficiency of 5.9%. In 2004, a DSC power station of 500W was demonstrated by IPP (Fig. 8).

2.3. Other commercial research on up-scaling technology of DSC

Many institutes and companies had developed the commercial research on up-scaling technology of DSC. Gifu University, Japan, developed colorful cells based on indoline dye and deposited with zinc oxide on large size of plastic substrate [33]. Toin University of Yokohama, Japan, fabricated the full-plastic DSC modules based on low-temperature coating techniques of TiO_2 photoelectrode [34]. Peccell Technologies, Elecsel Japan, and Konarka US, practiced the utility and commercialization study about flexible DSC module on polymer substrate [31,35]. Léclanche S A, Solaronix, Switzerland, developed outer-door production of DSC. INAP, Germany gained an efficiency of 6.8% on a 400 cm^2 DSC module [32]. STI had completed the fist pilot-plant construction of DSC in October 2002. The DSC roof of 200 m^2 built in Newcastle showed the perspective of DSC commercialization [36].

3. Stability research on DSC

Apart from the up-scaling technology, the stability research also has great impacts to realize the potential application of DSC.

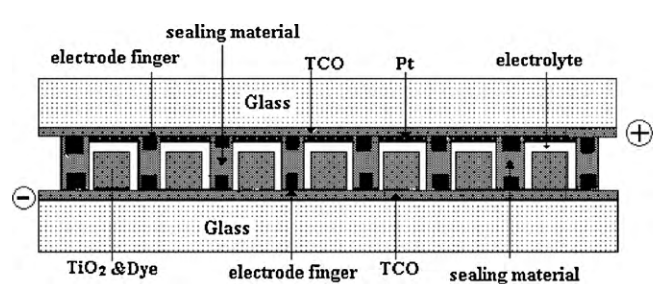


Fig. 7. Design scheme of parallel DSC module [10].



Fig. 8. Picture of the 500W DSC power demonstration in IPP, CAS [10].

According to the operating principle, preparation technology and material characteristics of DSC, it is potentially vulnerable to two main aspects:

1. Physical degradation. The system contains organic liquid which can leak out of the cells or evaporate at elevated temperatures. In principle, this can be overcomed using appropriate sealing materials and low volatility electrolytes. New type of polymers like Surlyn, Bynel, Himilan, ceramic glaze, and glass frit with different processing temperature had been applied. Several kinds of organic cations (alkyl imidazole cation, alkyl ammonium cation, etc.) and inorganic anions (BF_4^-, $AlCl_4^-$, PF_6^-, etc.) had been developed [37–39].
2. Chemical degradation. The dye and electrolyte in DSC will photochemically react or thermal degrade under working conditions of high temperature, high humidity, and illumination. The performance of DSC will irreversiblely decrease during the process causing the life time lower than the one required commercially (>20 years).

As there were no international standards specific in DSC testing, most of the research work had been carried out to identify the long-term stability of DSC according to IEC 61646 [40] and IEC 61215 [41] prepared for the testing of thin film photovoltaic modules and crystalline silicon photovoltaic modules, respectively. Some other studies also followed the national standards like JIS-C8938 (Japanese Industry Standard). In this section, indoor and outdoor tests carried out to identify the stability of DSCs and the large scale modules were presented.

3.1. Indoor stability tests on DSC

3.1.1. Light soaking test

The initial stability research on DSC had been carried out with respect to light soak some low power single cells. The samples exposed to simulated irradiation of 2.5 sun at spectrum of 400–800 nm showed a minor decrease in open circuit voltage (50 mV) as well as a slight increase in short-circuit current, after 8300 h of testing [42,43]. To avoid the thermal degradation impact to light soaking test, the samples were kept at constant temperature of 20 °C. In order to minimize the impact of DSC fabrication diversity to the test results, the masterplates prepared in the semi-automated processing line located in ECN were normally used by European researchers as the samples of stability tests (Section 2.2). ECN had reported a similar but less drop of performance on the single cells of 5.0 cm × 0.8 cm on the masterplates, after 8000 h light soaking under a relatively milder test, involving 1 sun illumination at 45 °C [21,44]. For comparison, the single cells on the masterplates did not show major changes in short-circuit current after a shorter time of test (approximately 1200 h), although the decrease in open circuit voltage for these cells during the test was approximately 10%, resulting in an overall decrease in efficiency of 12–15% [22]. The results obtained from the light soaking tests showed some striking differences in stability when different electrolyte solvents were used. The cells containing propionitrile showed better stability behavior compared to those with methoxyacetonitrile, after the tests under 1 sun illumination at 45 °C. The former showed a decrease in maximum power of less than 15% tested after 3400 h [21]. Many light soaking tests showed the generally used dye like N3 and N719 were stable when illuminated under medium light intensity at room temperature. In general, it is safe to say light soaking is not a dominant factor to address the degradation of DSC.

3.1.2. UV preconditioning test

UV preconditioning test should be taken with ultra–violet (UV) radiation before thermal annealing test/thermal cycling tests to identify those materials and adhesive bonds that are susceptible to UV degradation. The test performed by IVF showed UV light was deleterious for performance of DSC. Some low power monolithic modules without UV filters degraded fast and failed after 150 days when illuminated at 5000 lx with fluorescent light (Philips TLD 840). In contrast, the maximum power of the module protected by UV filters showed a slow degradation by approximately 7% [45]. The test taken by ECN showed the electrolyte additives could cause large difference in UV stability. When no electrolyte additives were used, the tested cells on masterplate demonstrated a dramatic drop of 50% in maximum power, after a 1500 h of UV irradiation at 38 °C. While some electrolyte additives like MgI_2 and CaI_2 showed strong enhancement to UV stability. The tested cells bleached indicating an irreversible consumption of I_2 in electrolyte. This might be explained by the side reactions of photogenerated oxidative holes at the TiO_2 surface and the corresponding electrons leading to a non-regenerative reduction of I_2 to I^-. The possible explanations for the enhanced stability of MgI_2 had been inferred as: a faster reduction of the holes by iodide; the lower photopotential; or the formation of a MgO surface layer, preventing side reactions [21].

3.1.3. Thermal annealing test

Thermal annealing test should be taken before thermal cycling test and damp heat test, in order to eliminate the thermal stress that might happen in the following tests. With the improvement of material and technology for DSC encapsulation, the physical degradation had been solved in such extent, that is, the electrolyte might not evaporate or leak out of the cell at the required thermal annealing temperature—85°C, which is required in IEC standard. However, the intrinsic chemical degradation will still happen during the test process.

It was revealed the long-term stability of DSC was related to the categories, components of electrolytes used and the dye applied. ECN reported the cells based on ionic liquids as solvents hardly degraded at 85 °C in dark, in contrast to ones with electrolytes based on acetonitrile or other organic solvents, though the initial efficiency of the former was substantially lower. For example the efficiency of the cell based on hexylmethylimidazolium iodide (HMI) was approximately 1–2% in sealed devices and 5% in open cells [22]. Compared to methoxyacetonitrile, propionitrile demonstrated better thermal stability. The cells with methoxyacetonitrile degraded strongly when test temperature was over 45 °C. The hydrolysis of methoxyacetonitrile, methoxyacetamide, was formed in the cells which were detected by gas chromatography–mass spectroscopy (GC–MS), after 435 h thermal annealing test in dark. With the increase of the time for thermal annealing, the position of main peak of the phase was shifted towards higher frequencies measured by electrical impedance spectroscopy (EIS), indicating a decrease in lifetime of photogenerated electrons in TiO_2 conduction bond [21,46]. Fujikura Ltd. operated the test with cells in which methoxyacetonitrile was applied as an electrolyte

solvent and Himilan (Dupont-Mitsui Polychemicals) as sealant. After 500 h thermal annealing at 85 °C, leaked components were detected and the performance of the cell was completely diminished [47]. The electrolyte that resulted in a more stable behavior contained an increased concentration of I_2 and did not contain *tert*-butyl pyridine (TBP) and LiI, N-methyl-benzimidazole (NMBI) had been used instead of TBP [22]. An amphiphilic dye Z907 with bopyridyl ligand replacing of long alkyl chains in N719, derived at EPFL, were more hydrophobic and showed good thermal stability while retaining good performance. The cells in which Z907 was applied as the dye retained 94% of the initial performance after 1000 h annealing at 80 °C [48].

Research showed the higher annealing temperature caused the more severe degradation. A depressed result displayed the combination of illumination and high temperature lead to more dramatic decrease of performance than high temperature alone, since only the former reflected a realistic outdoor condition. To disclose the effect of illumination to thermal annealing result, illumination/thermal annealing cycling test were designed. The result revealed the initial decrease at annealing temperature was reversible, which could be compensated in the following illumination process. The mechanism for degradation/recovery behavior had been inferred to the adsorption/desorption of dye on TiO_2 film [22].

3.1.4. Thermal cycling test

Thermal cycling test was designed to determine the ability of the module to withstand thermal mismatch, fatigue and other stresses caused by changes of temperature. The range of the testing temperature was between −40 and 85 °C, together with the requirements of cycling rate and cycling time, in IEC 61646 norm. FMF performed the test on the fabricated Z-type serial DSC modules of 30 cm × 30 cm to examine the thermal and mechanical stability of glass frit seal and Z-contact. The resistance of the serial connection was recorded to follow the trend of cycling temperature from −40 to 80 °C. For 50 cycles (250 h) no degradation was observed [11]. According to JIS-C8938 standard, endurance tests were carried out by Fujikura Ltd. to investigate the stability of the fabricated DSC modules with current collecting Ag grids. It was showed the cell performance was almost not deteriorated but slightly improved under the heat and cool cycle stress (−40 and 90 °C) for more than 200 cycles (800 h) [47].

3.1.5. Damp heat test

Damp heat test was designed to determine the ability of the module to withstand the effects of long-term penetration of humidity. The test temperature, relative humidity and the test duration were defined as 85 °C, 85%RH and 1000 h by referring to IEC 61646 standard. Researchers in EPFL disclosed humidity had a serious impact on cell performance and stability. The thermal stress caused by wet components at high temperature could destroy the seal, lead to desorption of dye from TiO_2 film and accelerate the side reactions [49]. Even the moisture intrusion into the cell during the assembling process could enhance the desorption or degradation of sensitizing dye reported by Fujikura Ltd. Experiment showed sells displayed stable short-circuit currents if cells were assembled under dry air (relative humidity/RH < 10%) or Ar (RH < 0.1%). In the later case the short-circuit currents of the cells were almost keeping constant after working for 800 h. While, the photocurrent decreased for about 40% when the cell was assembled under ambient atmosphere without humidity control (50–60% RH). For the damp heat tests carried out with the fabricated 5 cm × 5 cm-sized cells under condition of 85 °C, 85%RH, both gradual increase of short-circuit current and decrease of open circuit voltage were observed at the earlier stage of the test until about 300 h, and then every parameter became almost constant. Conversion efficiency showed almost no alteration during the test, and the degree of decrease was only 6% after about 1400 h [47].

3.2. Outdoor stability tests on DSC

The longest outdoor stability test in the world was performed by Toyota and Asin with the fabricated monolithic serial DSC modules for approximately 2.5 years. The result showed the short-circuit current gradually increased as the outdoor exposure time proceeded until 0.4 years, and then it was almost stabilized for 2 years. This indicated the function of the photoelectrode, that is, N719 dye-adsorbed TiO_2 film might be maintained. The open voltage and the fill factor gradually decreased as the outdoor exposure time proceeded which may related to the increase of the leak current fromTiO_2 to electrolyte. A slightly degradation of the efficiency was measured for -1.7×10^{-4} day^{-1}. Raman spectroscopy and electrochemical impedance spectrum revealed the photoelectrode and the carbon counter-electrode were almost stable, while some luminescent ingredients were generated in the electrolyte [50]. Asin and Toyota also investigated the possible challenge for outdoor practical use of DSC. The outdoor performance of large scale DSC modules had been examined for a half year. The report suggested DSC modules yearly generated 10–20% more electricity than conventional crystalline silicon modules of the same rated output power independent of the testing environment [51] This may relate to a higher actual efficiency of DSC compared to a rated one if cells are presented under the practical outdoor working condition, such as a elevated temperature or a higher proportion of diffusion, showing a remarkable priority of DSC.

4. Conclusion and perspective

DSC has great promise for the future to provide a combination of energy and natural light for prosperity. To realize the potential application of DSC, besides the efficiency should be further improved that may derive from new material and technology, the challenges for commercialization should also been considered in aspects of up-scaling, long-term stability, costs and potential markets. In this article, the design methods for large scale DSC modules had been introduced. The stability of the fabricated DSCs and large modules was identified in indoor and outdoor tests. However, it should be pointed out, these tests were inadequate to confirm the stability of DSC, since several tests such as wet leakage current test, humidity freeze test, etc. that required in IEC 61646, which are closely related to the performance of DSC, have not been implemented by far. On the other hand, the results obtained from the research on DSC stability are also suspectful as were derived from the test referring to the standards which cannot reflect the overall characteristics of DSC performance sufficiently and accurately. Therefore, to realize the potential markets and compete with silicon industry, it is urgent for the standards specific in DSC stability testing to be prepared, to guide the research on new materials, technology and up-scaling methods, and to realize the lifetime of 20 years for DSC products with a stable efficiency up to 6%.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Project number 20573038) and the Program for New Century Excellent Talents in University of China (NCET-07-0312).

References

[1] O'Regan B, Grätzel M. A low-cost high-efficient solar cell based on dye-sensitized colloidal TiO_2 films. Nature 1991;353(6364):737–40.

[2] Grätzel M. Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. J Photochem Photobiol A Chem 2004;164:3–14.
[3] Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, et al. Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers. J Am Chem Soc 2005;127(48): 16835–47.
[4] Green MA, Emery K, King DL, Hisikawa Y, Warta W. Solar cell efficiency tables (version27). Prog Photovolt Res Appl 2006;14:45–51.
[5] Chiba Y, Islam A, Han LY. Dye-sensitized solar cells with conversion efficiency of 11.1%. Jpn J Appl Phys 2006;45(25):638–44.
[6] Han LY, Fukui A, Fuke N, Yamanaka R. High efficiency of dye-sensitized solar cell and module. In: Proceedings of the 32nd IEEE photovoltaic specialists conference (PVSC) and fourth IEEE world conference on photovoltaic energy conversion (WCPEC); 2006. p. 625–30.
[7] Grätzel M. Dye-sensitized solar cells. J Photochem Photobiol C Photochem Rev 2003;4:145–53.
[8] Shi XZ, Wang L, Xi QG. The influence of local shunt current on the characteristics of junction of solar cells. Acta Energiae Sol Sinica 1999;20(2):209–15. (in Chinese).
[9] Spath M, Sommeling PM, Von Roosmalen JAM, Smit HJP, Burg NPG, Mahieu DR, et al. Reproducible manufacturing of dye-sensitized solar cells on a semi-automated baseline. Prog Photovolt Res Appl 2003;11:207–20.
[10] Dai SY, Weng J, Sui YF, Chen SH, Xiao SF, Huang Y, et al. The design and out door application of dye-sensitized solar cells. Inorg Chim Acta 2008;361:786–91.
[11] Sastrawan R, Beier J, Belledin U, Hemming S, Hinsch A, Kern R, et al. A glass frit-sealed dye solar cell module with integrated series connections. Sol Energy Mater Sol Cells 2006;90:1680–91.
[12] Hopkins JA, Phani G, Skryabin IL. Methods to implement interconnects in multi-cell regenerative photovoltaic photoelectrochemical devices. US Patent 6,555,741; 2003.
[13] Han LY, Fukui A, Chiba Y, Islam A, Komiya R, Fuke N, et al. Integrated dye-sensitized solar cell module with conversion efficiency of 8.2%. Appl Phys Lett 2009;94(1). 013305-1-3.
[14] Tulloch GE. Light and energy-dye solar cells for the 21st century. J Photochem Photobiol A Chem 2004;164:209–19.
[15] Fukui A, Fuke N, Komiya R, Koide N, Yamanaka R, Katayama H, et al. Dye-sensitized photovoltaic module with conversion efficiency of 8.4%. Appl Phys Express 2009;2. 082202-1r-r082202-3.
[16] Kay A, Grätzel M. Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. Sol Energy Mater Sol Cells 1996;44:99–117.
[17] Scholten MJ, Velt AC. Environmental LCA of large area dye sensitized solar modules. In: Proceedings of the 22nd European photovoltaic solar energy conference; 2007. p. 2683–7.
[18] Grätzel M. Perspectives for dye-sensitized nanocrystalline solar cells. Prog Photovolt Res Appl 2000;8:171–85.
[19] Takeda Y, Kato N, Higuchi K, Takeichi A, Motohiro T, Fukumoto S, et al. Monolithically series-interconnected transparent modules of dye-sensitized solar cells. Sol Energy Mater Sol Cells 2009;93:808–11.
[20] Kroon JM, Bakker NJ, Smit HJP, Liska P, Thampi KR, Wang P, et al. Nanocrystalline dye-sensitized solar cells having maximum performance. Prog Photovolt Res Appl 2007;15:1–18.
[21] Hinsch A, Kroon JM, Kern R, Uhlendorf I, Holzbock J, Meyer A, et al. Long-term stability of dye-sensitized solar cells. Prog Photovolt Res Appl 2001;9:425–38.
[22] Sommeling PM, Spath M, Smit HJP, Bakker NJ, Kroon JM. Long-term stability testing of dye-sensitized solar cells. J Photochem Photobiol A Chem 2004;164:137–44.
[23] Okada K, Matsui H, Kawashima T, Ezure T, Tanabe N. 100 mm × 100 mm Large-sized dye sensitized solar cells. J Photochem Photobiol A Chem 2004; 164:193–8.
[24] Dai SY, Wang KJ, Weng J, Sui YF, Huang Y, Xiao SH, et al. Design of DSC panel with efficiency more than 6%. Sol Energy Mater Sol Cells 2005;85:447–55.
[25] Dai SY, Wang KJ. Optimum nanoporous TiO_2 film and its application to dye-sensitized solar cell. Chin Phys Lett 2003;20(6):953–60.
[26] Dai SY, Xiao SF, Shi CW, Cheng SH, Huang Y, Kong FT, et al. Electrolyte optimization in dye-sensitized solar cells. Chem J Chin Univ 2005;26: 518–21 (in Chinese).
[27] Dai SY, Cheng SH, Xiao SF, Shi CW, Huang Y, Kong FT, et al. Effect of temperature on DSC modules performance with different solvents in electrolyte. Chem J Chin Univ 2005;26(6):1102–5 (in Chinese).
[28] Dai SY, Weng J, Sui YF, Shi CW, Huang Y, Cheng SH, et al. Dye-sensitized solar cells, from cell to module. Sol Energy Mater Sol Cells 2004;84:125–33.
[29] Dai SY, Wang KJ, Sui YF, Weng J, Huang Y, Hu LH, et al. Design and assembly of dye-sensitized solar cell module. Acta Energiae Sol Sinica 2004;25(6):807–10 (in Chinese).
[30] Weng J, Xiao SF, Chen SH, Dai SY. Research on the dye-sensitized solar cell module. Acta Phys Sin 2007;56(6):3602–6 (in Chinese).
[31] Wang KJ, Dai SY. The research progress in dye-sensitized nano-film solar cells. In: Proceeding of the 8th China photovoltaic conference. 2004. p. 57–62 (in Chinese).
[32] Kong FT, Dai SY. Dye-sensitized solar cells. Prog Chem 2006;18(11):1409–24 (in Chinese).
[33] Yoshida T, Oekermann T, Peter LM, Minoura H, Wijayantha KGU. Electrodeposition of nano-structured porous crystalline ZnO/dye hybrid thin films for plastic solar cells. In: The 16th international conference of photochemical conversion and solar storage; 2006.
[34] Miyasaka T, Kijitori Y, Ikegami M. Fabrication of full-plastic dye-sensitized solar cell modules based on low-temperature coating techniques. In: The 16th international conference of photochemical conversion and solar storage; 2006.
[35] Tian HM, Liu B, Yu T, Zou ZG. Analysis of dye-sensitized solar cells industrialization progress. World Sci-tech R&D 2008;30(1):49–55 (in Chinese).
[36] Robert F. Tricks for beating the heat help panels see the light. Science 2003;300:1219–23.
[37] Chmiel G, Gehring J, Uhlendorf I, Jestel D. Dye sensitized solar cells (DSC): progress towards application. In: Proceedings of the 2nd world conference and exhibition on photovoltaic solar energy conversion; 1998. p. 53–7.
[38] Hinsch A, Wolf M. Method of manufacturing a module of photoelectrochemical cells with long-term efficiency. Patent publication number WO9629715; 1996.
[39] Kurch M. Solar module. Patent publication number WO0046860; 2000.
[40] IEC61646 International Electrotechnical Commission. Thin-film terrestrial photovoltaic(PV) modules—design qualification and type approval; 2008.
[41] IEC61215 International Electrotechnical Commission. Crystalline silicon terrestrial photovoltaic (PV) modules—design qualification and type approval; 2005.
[42] Kohle O, Grätzel M, Meyer AF, Meyer TB. The photovoltaic stability of bis(isothiocyanoto) Ru(II)-bis-2,2′-bipyridine-4,4′-dicarboxylic acid and related sensitizers. Adv Mater 1997;9:904–6.
[43] Rijinberg E, Kroon JM, Wienke J, Hinsch A, Von Roosmalen JAM, Sinke WC, et al. Long-term stability nanocrystalline dye-sensitized solar cells. In: Proceedings of the 2nd world conference PVSEC; 1998. p. 47–52.
[44] Hinsch A, Kroon JM, Späth M, Von Roosmalen JAM, Bakker NJ, Sommeling PM, et al. Long-term stability of dye sensitized solar cells for large area power applications (LOTS-DSC). In: Proceedings of the 16th European photovoltaic solar energy conference; 2000. p. 32–8.
[45] Pettersson H, Gruszecki T, Johansson LH, Johander P. Manufacturing method for monolithic dye-sensitized solar cells permitting long-term stable low-power modules. Sol Energy Mater Sol Cells 2003;77:405–13.
[46] Burnside S, Winkel S, Brooks K, Shklover V, Grätzel M, Hinsch A, et al. Deposition and characterization of screen-printed porous multi-layer thick film structures from semiconducting nanomaterials for use in photovoltaic devices. J Mater Sci Mater Electron 2000;11:355–62.
[47] Matsui H, Okada K, Kitamura T, Tanabe N. Thermal stability of dye-sensitized solar cells with current collecting grid. Energy Mater Sol Cells 2009;93: 1110–5.
[48] Wang P, Zakeeruddin SM, Moser JE, Nazeeruddin MK, Sekiguchi T, Grätzel M. A stable quasi-solid-state dye-sensitized solar cell with an amphiphilic ruthenium sensitizer and polymer gel electrolyte. Nat Mater 2003;2:402–7.
[49] Grätzel M. Photovoltaic performance and long-term stability of dye-sensitized meosocopic solar cells. CR Chimie 2006;9:578–83.
[50] Kato N, Takeda Y, Higuch K, Takeichi A, Sudo E, Tanaka H, et al. Degradation analysis of dye-sensitized solar cell module after long-term stability test under outdoor working condition. Sol Energy Mater Sol Cells 2009;93:893–7.
[51] Toyoda T, Sano T, Nakajima J, Takeichi A, Sudo E, Tanaka H, et al. Outdoor performance of large scale DSC modules. J Photochem Photobiol A Chem 2004;164:203–7.

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